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## TECHNIQUES FOR INVESTIGATING STRUCTURE AND COMPOSITION WITH HIGH SPATIAL RESOLUTION

JOHN B. VANDER SANDE

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

### ABSTRACT

The techniques of scanning transmission electron microscopy and field ion microscopy/atom probe are briefly described. The advantages of these techniques for high spatial resolution compositional analysis are discussed and examples cited.

### INTRODUCTION

One of the major benefits expected from rapid solidification processing is a refinement of the microstructure and a reduction in segregation in alloys processed in this way. The finer scale to the microstructure developed by rapid solidification processing places extreme demands on the techniques available for elucidating the details of these microstructures.

This paper discusses two instrument types that are capable of high spatial resolution compositional analysis: the scanning transmission electron microscope (STEM) and the field ion microscope/atom probe (FIM/AP). After describing each technique, including a brief description of limitations, examples of microstructural analysis from each will be presented.

### STEM

The field emission STEM used in this work was a VG Microscopes HB5 commercial instrument, fitted with an energy dispersive X-ray analysis system and an electron energy loss spectrometer. The electron source is a cold tungsten field emitter. There is a two-lens electron probe forming system, by which typically 2 nA of 100 kV electrons can be formed into a probe approximately 1.5 nm diameter on the specimen. The vacuum in the specimen chamber is  $\sim 2 \times 10^{-9}$  torr, which minimizes any problems of specimen contamination. The X-ray detector is a slightly modified Kevex Si (Li) detector, with a Kevex 7000 multichannel analyzer and microcomputer system for spectral manipulation.

Specimens in the STEM consist either of thin sections of bulk material, or carbon films supporting particulate material. While it is possible to image specimens many tens to several hundred nanometers thick, effects such as beam spreading, specimen fluorescence, and absorption become of increasing importance in modifying the resolution and sensitivity of X-ray analysis.

Interpretation of energy-dispersive X-ray data requires a great deal of care. The usual way to consider the effects of X-ray production is to employ the sensitivity factor method due to Cliff and Lorimer (1), embodied in the equation:

$$\frac{C_A}{C_B} = \frac{I_A K_A}{I_B K_B} \quad (1)$$

where  $C_A/C_B$  is the ratio of the concentrations of the elements A and B in a specimen,  $I_A$  and  $I_B$  are the integrated X-ray counts in chosen lines due to each element, and  $K_A$  and  $K_B$  are sensitivity factors. Often the ratio  $K_A/K_B$  is used as a relative sensitivity factor denoted by  $K_{AB}$ , relating the sensitivities of the two elements. In this case, some element in the specimen is

chosen as the reference, and the relative sensitivity factors for each of the other elements are determined from measurements on specimens of known composition. It is thus possible to deduce the composition of the sample from the X-ray intensities. Strictly, the factor  $K$  is affected only by the beam voltage and the transitions giving rise to the X-rays. It is convenient, however, to consider also the effect of the detector geometry, and the absorption in the detector window, and to include them in the value of  $K$ , the disadvantage of this course of action being that the values of  $K$  become instrument-dependent.

If the X-rays were generated in an infinitely thin specimen in free space, then the measured X-ray signals would correspond exactly to the generated X-ray intensities. Such, however, is not the case, and it is necessary to consider (a) the modification to the X-ray intensities as they travel through adjacent material and selective absorption occurs, (b) generation of spurious X-rays from remote parts of the specimen and the microscope as a result of spurious radiation (electrons and X-rays) generated in the microscope column or as a result of interaction of the main electron beam with the specimen itself, and (c) spreading of the electron beam in the sample which degrades the spatial resolution for X-ray analysis.

For uniform thin foils, correction equations have been developed to allow for the effects of selective absorption (2). In such cases, fluorescence is usually of less importance. However, in multiphase materials the situation is not so simple. In general the X-ray path through each phase is not known, and the distance from the X-ray source to different fluorescing phases is not well characterized. Thus accurate correction of the X-ray intensities is not usually possible in such cases. To some extent the problems may be overcome by the use of extraction replica techniques, but these cannot be employed in cases where it is required to measure the compositions of, say precipitates and matrix in immediately adjoining regions. In such instances it is of some assistance to use specimen geometries in which the extent of interaction between the various phases is minimized.

It has been shown that in the HB5 STEM fitted with a "virtual objective aperture," the contribution of spurious radiation generated by the microscopy is negligible compared with that generated by the interaction of the beam with the specimen. Further, if the microscope is not so equipped, this "hole count" can simply be recorded by passing the beam through a hole in the specimen, and subtracting the resulting X-ray spectrum from that recorded while the beam is incident on a feature in the specimen. The main disadvantage of this latter procedure is the large increase in the background noise level.

The issue of electron beam spreading in the sample and the influence this has on X-ray spatial resolution is a complex question. Suffice it to say that smaller diameter electron probes, thinner samples, and higher electron accelerating potential all act to improve spatial resolution via energy dispersive X-ray analysis.

#### FIELD ION MICROSCOPE/ATOM PROBE

The time-of-flight atom probe used in this work has been described in detail elsewhere (3). The instrument consists essentially of two parts, a field ion microscope (FIM) section in which an atomic resolution image of the specimen is obtained, and a mass spectrometer section in which the chemical identity of ions field evaporated from the specimen surface is determined. A small aperture hole in the FIM imaging screen allows ions to enter the mass spectrometer section, and defines the area from which the chemical analysis is obtained. The time-of-flight principle is used to identify the ions. In this method, ions are removed from the specimen surface at well defined instants by the application of a train of nanosecond rise-time high voltage pulses, superimposed on

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the normal d.c. imaging voltage in the FIM. The ions are accelerated, and pass from the FIM section into a drift tube, at the end of which is situated a particle detector of single ion sensitivity. The mass-to-charge ratio ( $m/n$ ) can then be estimated for each ion from the following equation:

$$m/n = 0.19297 E t^2/z^2 \quad (2)$$

where  $E$  = the total potential through which the ion is accelerated (kV)

$t$  = flight time to detector ( $\mu$ s)

$z$  = flight path (m)

Flight times are measured using standard digital techniques. Up to four parallel timing channels are available, to allow for the possible evaporation of multiple ions on a single high-voltage pulse. The digital data is fed into a PDP11/10 minicomputer, which controls the experimental cycle, calculates and stores the mass spectra, and provides the operator with an ion-by-ion output of the composition of the specimen.

At first sight, a particular advantage of the atom probe technique is the simple, quantitative interpretation which is possible for the data on chemical composition. However, considerable care must be taken to establish the correct conditions for stable operations. For example, if the vacuum is poor, one or more chemical species on the specimen may be selectively etched away by reaction with chemically active gas molecules. Also, if the standing voltage on the specimen is too high, some species may be preferentially lost from the surface by d.c. field evaporation during the time interval between the application of successive high voltage pulses. In either case, errors will arise in the resultant chemical analysis, which is obtained only from ions desorbed during the period of the high voltage pulse. In the case of new or unfamiliar specimen materials, it is generally found desirable to run preliminary experiments in which the apparent chemical composition is measured as a function of the ratio of the pulse voltage to the d.c. standing voltage (the "pulse fraction"). A certain minimum pulse fraction, usually 15% or more, is needed in order to obtain consistent results. When suitable standard materials of known composition are available, these procedures can be extended to determine the absolute quantitative accuracy of the atom probe technique.

#### SPATIAL RESOLUTION

##### a) STEM

The factors influencing spatial resolution in the STEM are the size of the incident electron probe and the thickness of the sample if a fixed acceleration potential is assumed. While the image resolution is governed principally by the incident probe diameter (assuming ample signal-to-noise ratio and electron energy discrimination), X-ray microanalysis involves working with much poorer signal-to-noise ratios, leading to the employment of larger beam currents with larger beam sizes and increased beam broadening. In some cases, the form of the specimen renders these problems insignificant, as in the use of carbon extraction replicas, and in other areas corrections or deconvolutions are possible, as in segregation at grain boundaries. In general, however, each specimen must be considered separately, the need for correction determined and the data treated accordingly.

##### b) ATOM PROBE

The spatial resolution of the atom probe may be considered in two components, the "depth resolution" (i.e. in a direction perpendicular to the surface of the tip) and the "lateral resolution", in the plane of the surface being analysed. The lateral resolution is determined mainly by the size of the aperture in the

image screen assembly, divided by the magnification of the image. The minimum size of this aperture is governed by the required statistics in the data. Simply, the larger the aperture, the more atoms are recorded. It would be possible to use a variable geometry slit assembly, to match the aperture to the area of interest, but this would present formidable engineering difficulties, and has not yet been accomplished. A fixed aperture (physically, a hole in the channel plate) is used, and the magnification is adjusted by changing the distance from the tip to the channel plate. Typically, an aperture corresponding to a region 2-4nm in diameter on the specimen is used. The lateral spatial resolution may be degraded, however, in regions where non-uniform curvature of the tip (because, for instance, of second-phase particles) distorts the local electric field, leading to aberrations in the trajectories of the desorbed ions. If the atomic planes are nearly parallel to the local surface of the tip, the atoms tend to evaporate from the edge of the plane, giving the effect of the plane 'peeling back' from the edge. If the hole in the channel plate is sufficiently small that it does not extend from the edge of one plane to the next, then single atomic plane depth resolution is possible. In practice, this possibility is only useful if the tip can be pre-aligned so that the plane of interest (an interface, for example) is set parallel to the surface before analysis begins.

#### QUANTITATIVE ANALYSIS

##### a) STEM

A wide variety of problems, some instrumental and some specimen related, affect STEM X-ray measurements. These problems include: variations in tip current, generation of spurious radiation in the microscope leading to the so-called "hole count", varying sensitivity of the X-ray detector to X-rays of different energies, low signals because of small angles subtended at the specimen by the detector, signal-to-noise limitations because of bremsstrahlung background, spurious peaks because of detector anomalies (mainly escape peaks and sum peaks), specimen drift, differential polishing of different elements in an alloy, specimen contamination, reabsorption of emitted X-rays by the specimen, fluorescence of remote parts of the specimen by radiation generated by the specimen, and spreading of the beam by the sample. Some of these factors are fixed in a given instrument, and are therefore incorporated in empirically-determined K-factors, and some apply to all signals uniformly and hence only affect the counting statistics. Specimen drift can be corrected at intervals during an analysis, while contamination can usually be prevented by cleaning the specimen in an appropriate way. The hole count can either be measured and subtracted, or may be insignificant. During the analysis, therefore, the three most important variables are re-absorption of the emitted X-rays, fluorescence, and beam spreading. Each of these is minimised by making measurements on the thinnest possible regions. If the thickness is uniform and can be determined by, for example, convergent beam diffraction, and the specimen is homogeneous, then corrections can be made to allow for absorption. Usually, neither of these conditions is met, and then it is only possible to determine the likely range of the correction.

##### b) ATOM PROBE

Once the appropriate pulse fraction for a particular material has been determined the quantitative analysis capability of the atom probe is generally excellent. Very often statistical fluctuations in the number of counts recorded is the limiting problem. Consider for example, a singly atomic layer. If the specimen is adjusted for ideal conditions for single atomic layer detection, and if an aperture corresponding to 4nm on the specimen (at the large end of the typical range) is used, then <400 atoms will be analysed. If half of these are of element A and half of element B, then the total number of atoms of each is

200. As the standard deviation of this number of counts is 14, then the analysis result would give  $50 \pm 3.5\%$  of each element. Another difficulty comes from the limited mass-resolution of the time-of-flight spectrometer. If enough counts are obtained, deconvolution of adjacent mass peaks can be attempted, but otherwise it becomes very difficult to make quantitative measurements of small amounts of element Z + 1 in the presence of a large concentration of element Z. A similar difficulty arises if a multiply charged ion of one species has the same mass to charge ratio as a singly charged ion of another element.

#### EXAMPLES

##### a) STEM

The development of 303 stainless steel was motivated by the need for a free-machining stainless steel. By addition of large amounts of sulfur ( $\sim 0.15$  wt%) in combination with manganese, a manganese sulfide precipitate is formed during solidification. In conventional ingot processing of 303 stainless steel, these precipitates are large (100 micron long by 20 micron wide) cigar shaped particles strung out in the rolling direction of the material. These large, brittle precipitate particles limit the size of chips formed during machining operations which makes 303 stainless steel a free-machining grade of austenitic stainless steel.

Figure 1 shows a cellular structure in a thin foil of a rapidly solidified (centrifugally atomized) powder of 303 stainless steel. The particles delineating the cell boundaries have been shown by X-ray analysis in the STEM to be nominally MnS. Figure 2 presents a composition profile, generated by point-to-point analysis, across a cell wall in this structure. Note that there is an increase in Ni content and corresponding decrease in Fe content associated with the cell wall. The Cr content of these cells appear to be uniform. In addition, silicon concentration along the profile are countervariant with Mn behavior while changes in S concentration are covariant with Mn. The spatial resolution demonstrated in Figure 2 should be noted.

These observations of compositional variations occurring within rapidly solidified powders are being used (4) to analyze the solidification modes in these rapidly solidified steels.

##### b) ATOM PROBE

It is well known that small additions of alloying elements such as chromium, manganese or molybdenum can have a profound effect in retarding the rate of the pearlite reaction in carbon steels. It is of interest to determine the distribution of alloying elements after reaction at low temperatures, in order to obtain information about the factors which control reaction kinetics in this temperature regime.

The steel was austenitized for 1 hour at  $900^\circ\text{C}$ , and then isothermally transformed to pearlite in a salt bath held at  $597^\circ\text{C}$ . The reaction time was 2 minutes, and the samples were then water quenched. The minimum pearlite spacing obtained by this procedure was approximately 100nm. An atom probe composition profile across a ferrite-cementite interface is illustrated in Figure 3, and shows that just within the cementite phase the local chromium concentration is very strongly enriched, to a level of approximately 5%. The excellent spatial resolution available and the quantitative carbon analysis should be noted.

#### REFERENCES

1. G. Cliff and G. W. Lorimer, *J. of Micros.* **103**, 203 (1975).
2. J. I. Goldstein, *Introduction to Analytical Electron Microscopy* (eds. J. J. Hren, J. I. Goldstein and D. C. Joy), Plenum Press 1979.

3. M. K. Miller, P. A. Beaven and G. D. W. Smith, Surface and Interface Analysis, 1979, 1, 149.

4. T. F. Kelly, J. B. Vander Sande, and M. Cohen, these proceedings.

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500 nm

Figure 1: A STEM annular dark-field image of a thinned 303 stainless steel powder which has been rapidly solidified. The annular structure of this fcc particle is delineated by MnS precipitates which appear light gray in this image. The composition profile shown below as Figure 2 was obtained from a similar particle.

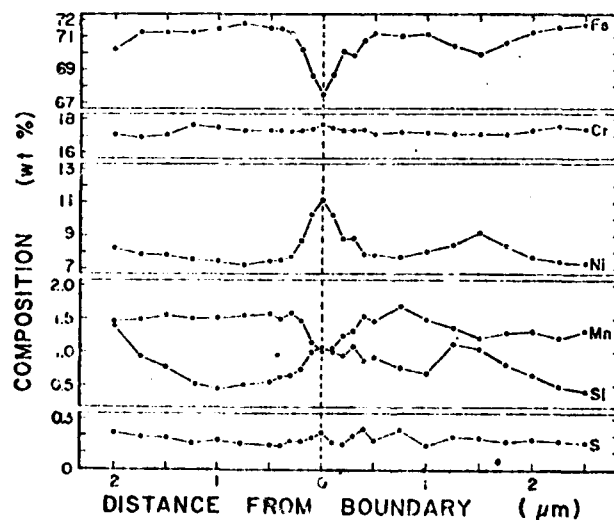


Figure 2: A composition profile constructed across a cell boundary in a rapidly solidified powder. Note the spatial resolution demonstrated in this profile obtained in the STEM.

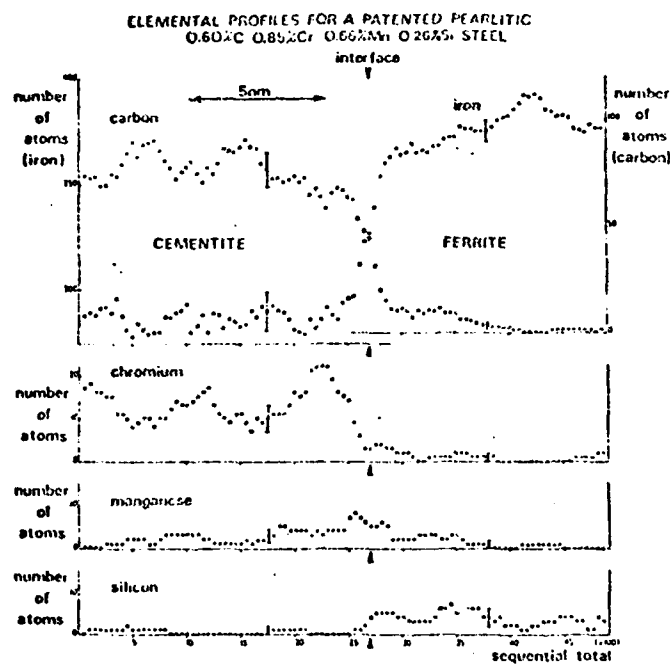


Figure 3: Atom probe composition profile across a cementite-ferrite interface in a chromium steel.

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